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STUDY OF GROWTH PARAMETERS FOR
REFRACTORY CARBIDE SINGLE CRYSTALS

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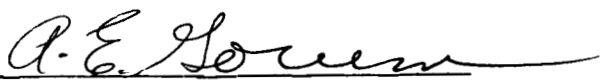
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Material Sciences Division

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I INTRODUCTION

Stanford Research Institute has been engaged by the National Aeronautics and Space Administration to determine the feasibility of growing refractory carbide single crystals, using relatively new solution and melt techniques. The materials of interest are hafnium carbide, tantalum carbide, and solid solutions of the two.

Up to the present time, major effort has been directed toward development of crystal growth facilities capable of providing the desired conditions and toward establishing, as nearly as possible, operating boundary conditions. In the course of this work, exploratory runs were of value, primarily, in pointing out operational difficulties and specific problem areas. Consequently, little materials information was obtained. During the period covered by this report, calculations of desired operating conditions were essentially completed, and initial attempts were made to evaluate the behavior of carbides under selected growth conditions.

II SUMMARY AND CONCLUSIONS

A considerable effort was devoted to utilization of available information on the properties of carbides at high temperatures to analyze theoretically their behavior during fusion crystal growth. Results, within the precision allowed by available data, indicate that it should be possible to maintain single phase compositions at the melting point. Polished sections and X-ray lattice constant measurements confirm that, under suitable conditions, carbides can be arc-melted without significant shifts in stoichiometry. It appears that control of the composition of the gaseous environment may permit significant variations in carbide stoichiometry within the single phase region.

As yet, melting of the carbides in the r-f plasma has not been attained. Power levels of 10 kw in an argon plasma have been attempted. Exploration of the effect of increasing hydrogen additions on heat transfer to the seed crystal is beginning. If melting is not obtained in this manner, the plasma power level will be increased further. Water-cooled plasma containment tubes made of quartz can now be operated successfully at 10-kw power levels.

Initial carbon solubility runs have been completed on germanium, germanium-10 atomic percent hafnium, aluminum-10 atomic percent hafnium, and iron-10 atomic percent hafnium alloys. As a result of these runs, germanium has been eliminated from consideration since it has not been possible to separate the carbide crystals from the solvent at the completion of a run. Carbon solubilities in the aluminum-hafnium alloy appear very close to those for silicon, which is employed for growth of silicon carbide crystals. Additional solubility studies on these alloys, containing different proportions of hafnium and tantalum, will be required before conditions can be selected for crystal growth attempts.

III CRYSTAL GROWTH STUDIES

A. Materials

Supplier's analyses of starting materials to be used in crystal growth studies are shown in Table I. Aluminum (99.5+%) employed in alloy studies was obtained from Kaiser Aluminum Company. The iron was a high purity (99.9+%) vacuum-cast grade obtained from National Research Corporation. Semiconductor grade germanium was purchased from Eagle Pitcher. The carbides for the initial melting studies discussed in this report, performed before the pure carbides were received, were obtained from Firth Sterling (HfC) and Kennametal (TaC). The purity of this HfC was reported as better than 98 percent. Spectrographic analysis showed boron to be a major impurity, along with lesser amounts of zirconium, titanium, iron, and calcium. HfB_2 was identified in the X-ray powder patterns of the starting material, but it was not observed after arc melting. Most likely it was incorporated into the HfC lattice during melting. This could lead to a slight reduction in the lattice constant ($a_0(\text{HfB}) = 4.62 \text{ \AA}$). No analyses were obtained for the TaC purchased from Kennametal.

B. Analytical Procedures

In attempting to establish suitable operating parameters for the growth of single crystals of a chemical compound, one must initially be concerned with the composition range over which a single phase may be maintained, and with how the exact chemical composition may be ascertained within this range. In the case of the carbides of interest in this investigation, measurement of the lattice parameter combined with direct observation of polished sections appears quite suitable. However, for tantalum carbide, particularly, although the change in lattice parameter is large enough to provide excellent sensitivity, there is considerable disagreement in the literature about the correlation of lattice constant and composition. A number of the relations reported are shown in Fig. 1. The variability of results undoubtedly arises largely from impurities in available materials, particularly oxygen and nitrogen, since the suboxide and nitride form solid solutions with the carbide. Actually, the agreement of results of Sara,⁴ Bowman,⁵ and Lesser⁶ is surprisingly good, and these values will be used in this investigation. In addition, these investigators agree quite closely that the phase boundaries are at about 41.5 atomic percent carbon and 49.5-50 atomic percent carbon.

Table I

SUPPLIER'S ANALYSES OF STARTING MATERIALS*

Elements	HfC ^a (ppm)	TaC ^a (ppm)	Ta ^a (ppm)	Hf ^b (ppm)
Al	34	< 10	< 10	37
B	5	< 1	< 1	< 0.2
C	6.30%	6.33%	80	--
Cb	--	< 50	< 50	--
Cd	< 1	< 1	< 1	< 1
Co	< 5	< 5	< 10	< 5
Cr	50	< 10	< 10	< 10
Cu	< 40	< 2	< 5	< 40
Fe	360	62	115	73
Mg	< 10	< 10	< 10	< 30
Mn	< 10	< 10	< 10	< 10
Mo	80	< 10	< 10	< 10
N	325	80	45	10
Ni	100	< 10	< 10	< 10
O	640	250	600	930
Pb	< 5	< 5	< 10	< 5
Si	400	< 10	25	< 40
Sn	< 20	< 10	40	< 10
Ti	1500	< 10	< 10	< 20
V	10	< 10	< 10	5
W	< 20	37	< 10	< 20
Zr	0.78%	--	< 50	2.1%
Zn	--	< 25	< 10	--
Cl	--	--	--	280

* Wah Chang Corporation

^a -325 mesh powder

^b sponge

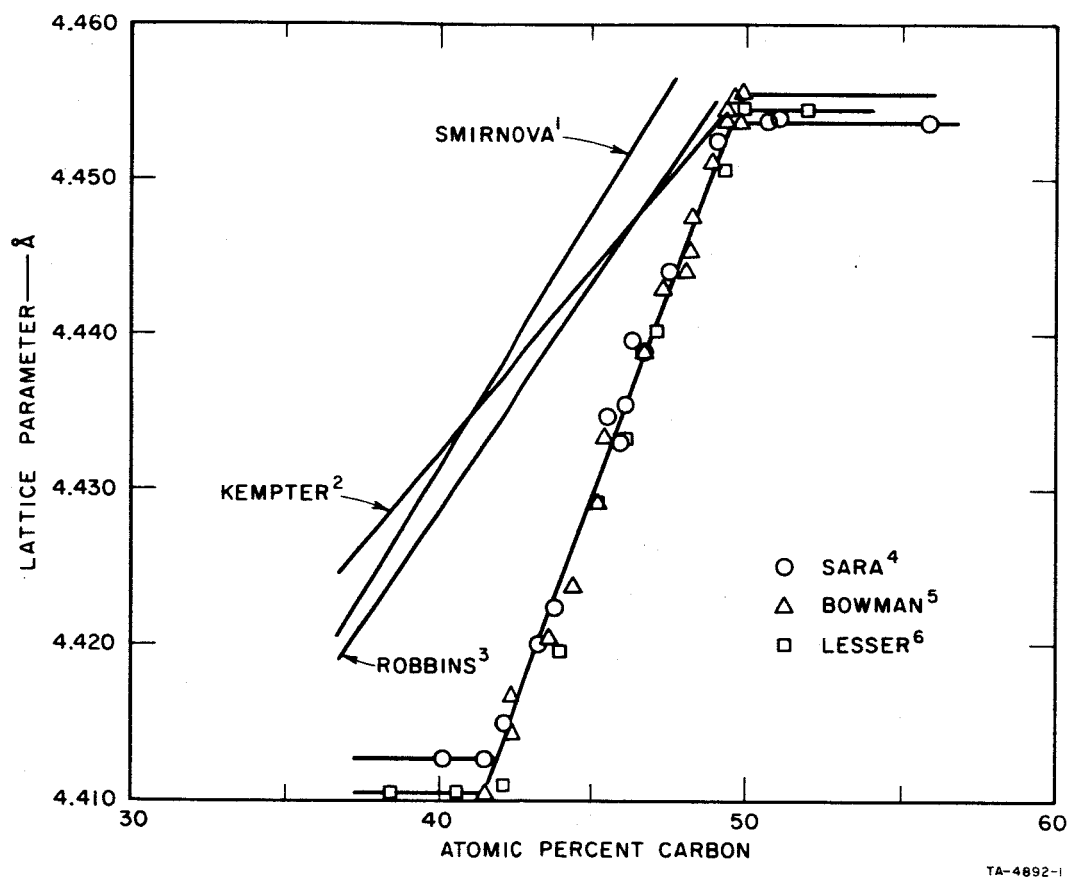


FIG. 1 VARIATION OF LATTICE PARAMETER WITH CARBON CONCENTRATION IN TaC

Values reported for the lattice parameters of HfC are shown in Fig. 2. Sara et al.⁸ report the homogeneous HfC field boundaries to be at 36.0 and 49.3 atomic percent carbon at 3150°C and at 34.5 and 48.0 atomic percent carbon at 2250°C, while Benesovsky and Rudy¹⁰ report 37 and 50 atomic percent carbon at 1550°C.

One would anticipate that crystals grown at low temperatures-- particularly if grown in the region of half the melting temperature-- should lie closer to the stoichiometric composition than those grown from a melt. In addition, thermally induced defect concentrations should be considerably reduced.

C. Stoichiometry Variations at Elevated Temperatures

A considerable amount of data has accumulated on vaporization rates, composition of vapors, and shift in composition for various carbides at elevated temperatures. In the course of this program this information has been evaluated and applied to the purpose of growing single crystals of hafnium carbide, tantalum carbide, and their solid solutions. Because considerably more is known about tantalum carbide than the others, it will be discussed first, including possible methods for control of composition by controlling the gas composition (i. e., acetylene-hydrogen mixture). This is followed by a briefer discussion of hafnium carbide. TaC-HfC solid solutions will be discussed in a subsequent report.

1. Vapor Pressure of Tantalum Carbide

The total vapor pressure of tantalum carbide, essentially carbon, has been calculated from vaporization data by Hoch¹² and by Coffman.¹³ These agree and are shown as a single line in Fig. 3, but the results have the inherent experimental disadvantage that the vapor pressure decreases with decrease in carbon concentration, and the results at the higher temperatures are for a lower average carbon ratio than are those obtained at the lower temperatures. The calculated lines by Kaufman¹⁴ at 46 and at 50 atomic percent carbon have a steeper slope than the experimental data.^{12,13} The straight lines have been extended to temperatures around 4000°K.

The effect of sample composition on the vapor pressure can be seen easier in Fig. 4, which gives the vapor pressures of tantalum and carbon at 2730°C (3000°K) and 4000°C above the phase diagram by Sara.⁴ The vapor pressure data at 2730°C for the solid is taken from Kaufman¹⁴ for the range of 41 to 51 atomic percent carbon. Nearly all

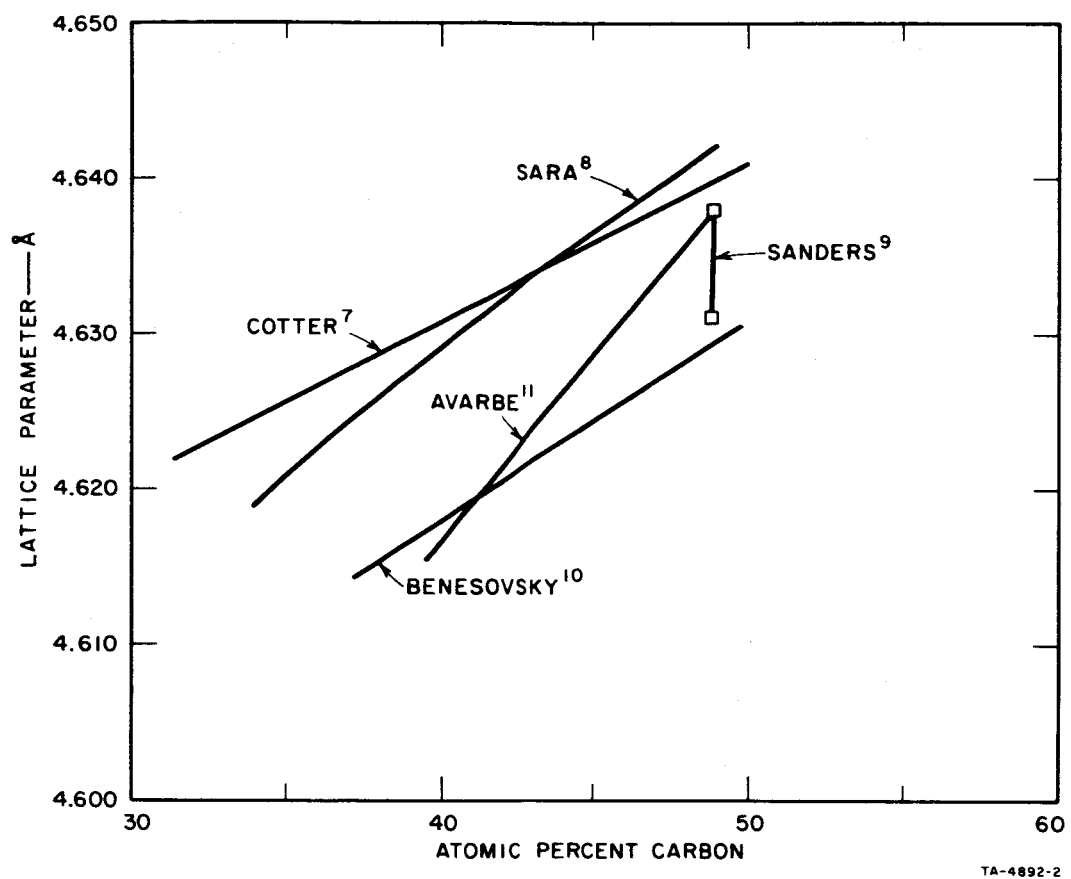


FIG. 2 VARIATION OF LATTICE PARAMETER WITH CARBON CONCENTRATION IN HfC

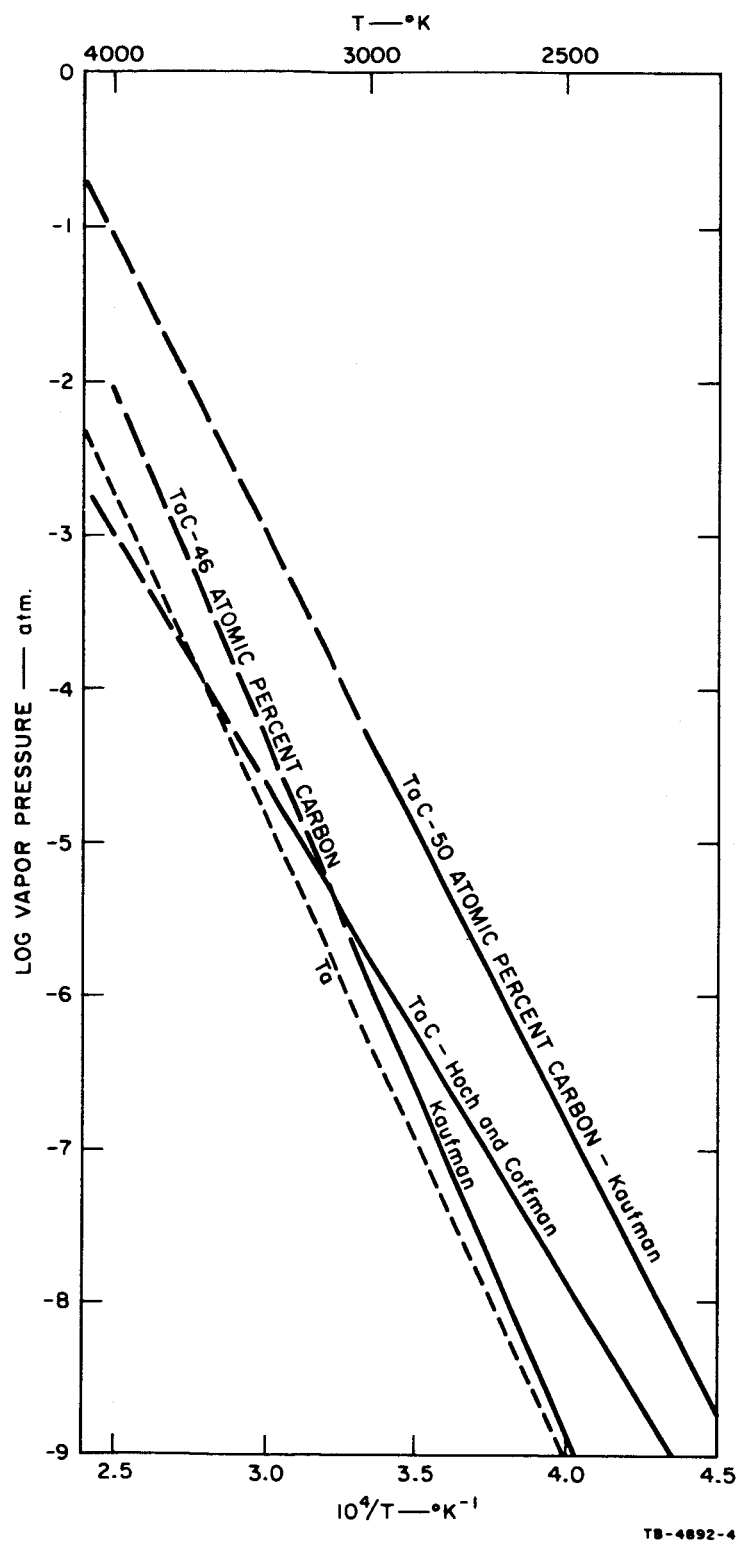


FIG. 3 VAPOR PRESSURE OF TANTALUM CARBIDE

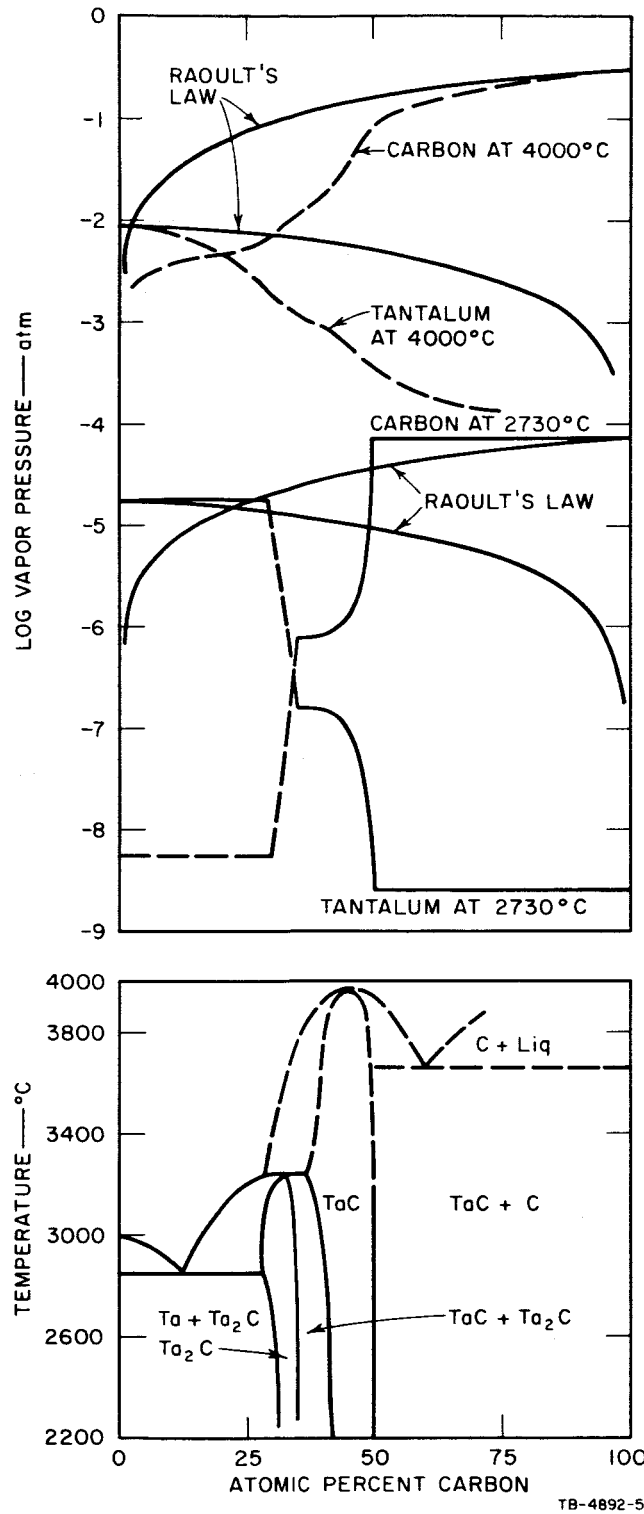


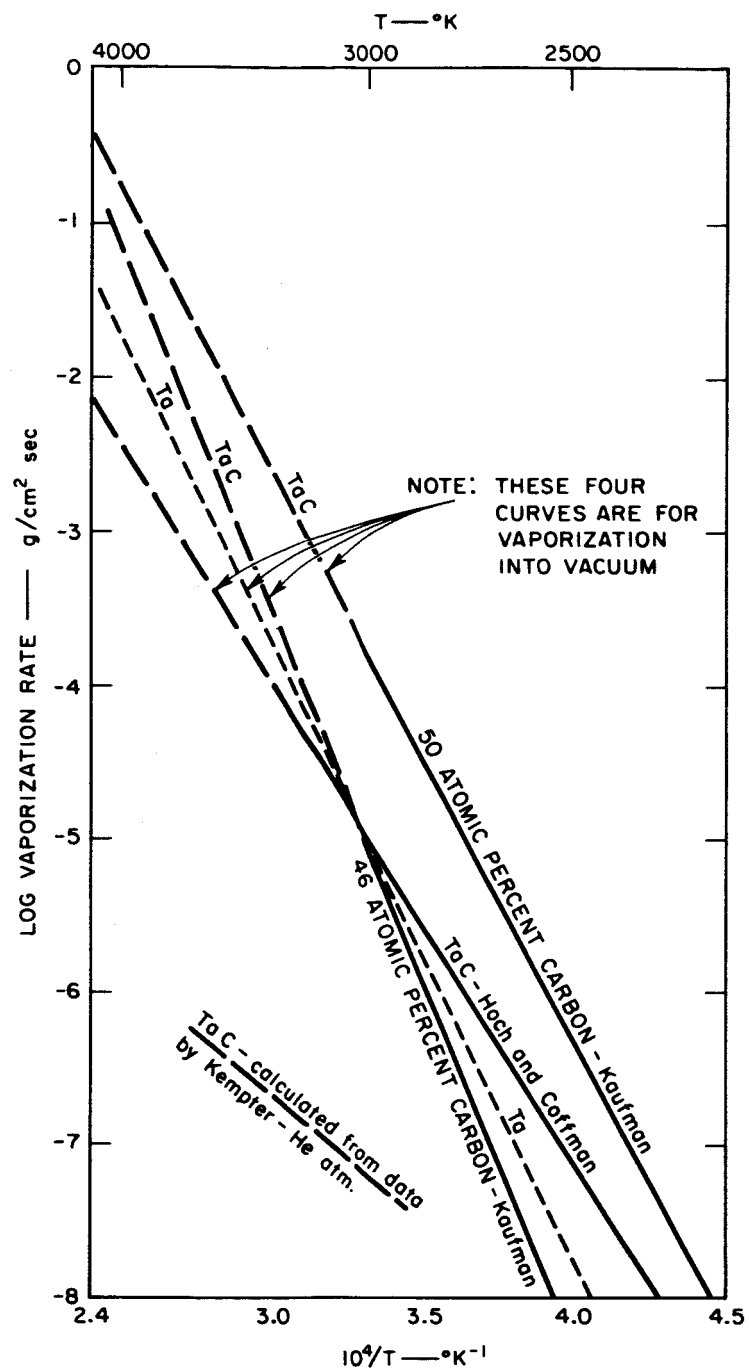
FIG. 4 PHASE DIAGRAM AND VAPOR PRESSURES OF Ta-C SYSTEM

of the remaining vapor pressure curves should be considered as schematic rather than as having the correct magnitude. The vapor pressure curves that would apply if Raoult's Law were obeyed are shown, and the curves for the liquid at 4000°C are shown as deviating less than the vapor pressure curves for the solid at 2730°C . The position of the melting point in the TaC region would have some effect on the vapor pressure curves at 4000°K , and many phase diagrams are shown with the maximum at 50 atomic percent carbon rather than at 45 to 46 percent as shown in Fig. 4.

2. Vaporization Rate of Tantalum Carbide

Most of the vaporization studies reported in the literature to date have been into vacuum and all have been below the temperature of the TaC-C eutectic, which occurs at about 3300°C . Studies in vacuum by Hoch¹² from 1960°C to 2490°C and Coffman¹³ from 2360°C to 3110°C agree and are discussed by Eberle.¹⁵ The data by Hoch and Coffman at the higher temperatures are for a lower average carbon ratio than those at the lower temperatures. Kaufman¹⁴ has calculated the vaporization rates, and his data are shown in Fig. 5 for tantalum carbide containing 46 and 50 atomic percent carbon. These data require a considerable extrapolation to reach the melting point of about 3800°C (4070°K).

The only study of vaporization into an inert atmosphere was by Kempter and Nadler,¹⁶ from 1890°C to 3320°C . However, they published only the decrease in the molar ratio of C/Ta and did not publish weight loss. Assuming that the loss of tantalum was negligible relative to carbon, we can calculate vaporization rates. (Note: Fries¹⁷ discusses Kempter's data on niobium carbide and gives the percent losses in weight, and these results vary from 1.1 to 2.0 times the values that we calculate from the decrease in carbon.) The vaporization rates calculated from Kempter's data at 2715°C to 3320°C are plotted in Fig. 5, but these should be considered as approximate values. Kempter's data at lower temperatures (2525°C to 1890°C) had the same rate as at 2715°C , possibly due to an initial loss for the reaction of the oxide impurity with carbon. Also, longer time studies at 3000°C gave markedly lower vaporization rates than for the short times, possibly due to the high initial losses being averaged over a longer period of time. The vaporization rate in an inert atmosphere should roughly parallel that in vacuum in the temperature range up to about 3500°K . Also both rates should have a gradually decreasing slope as the temperature approaches the boiling point, owing to a decrease in the rate of diffusion and in the effect of the vaporization products, acting as a diffusion barrier. The vaporization rate in vacuum would have a greater decrease than that in an inert atmosphere.



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FIG. 5 VAPORIZATION RATE FOR TANTALUM CARBIDE

a. Effect of Specimen Shape

In addition to temperature and sample composition, other factors that influence the vaporization rate include the diameter or shape of the sample, the composition of the inert gas, and the pressure of the inert gas. These factors have been studied by Jones¹⁸ and by Fonda^{19,20} for tungsten filaments. In general, they consider that volatilization occurs by diffusion of the gaseous molecules through a stagnant film in which the equilibrium composition is present at the solid-gas interface, and the concentration of the volatilizing species may be negligible at the outer boundary of the film. If volatilization occurs from a filament, the rate increases with decrease in diameter owing to a decrease in the film thickness or to a lower probability that a given atom entering the gaseous film will return to the solid (or liquid) surface.

The equation relating the filament diameter to vaporization rate is

$$m = \frac{\text{constant}}{a \log_e b/a}$$

where m = vaporization rate, a = filament diameter, and b = gas film diameter. The value of b is calculated from the equation $\ln b/a = 2B/b$, where B is the film thickness over a plane surface (a value of 0.43 cm was used¹⁹). From this, the evaporation of a 0.2-cm-diameter wire is 2.1 times that of a 1-cm-diameter wire, while the 1-cm wire has an evaporation rate close to that of a flat surface. The vaporization from a tip of a rod would be affected similarly, probably with a larger difference. Since the seed crystal for carbide melt growth will be at least 0.2 cm in diameter and will be widened rapidly to greater than 1 cm, it does not appear that this factor will have a significant effect on vaporization.

b. Effect of Inert Gas Composition

The choice of inert gas has an effect on the diffusion coefficient which affects the vaporization rate. For this application the equation by Wilke and Lee²¹ was used. A knowledge of the molecular volume of the liquid at the normal boiling point is required but is not known for tantalum. Arbitrary values of 50 and 100 cc/g-mole were used for the molal volume of tantalum and gave little difference in the calculated values of the diffusion coefficient. The calculated diffusion coefficients of mixtures of carbon in hydrogen or argon and of tantalum in hydrogen and argon are given in Table II. In the case of carbon, the predominant equilibrium species is triatomic carbon, but monatomic carbon is

Table II
DIFFUSION COEFFICIENTS AT 3000°K

	V_0 (cc/g-mole)	D in H ₂ (cm ² /sec)	D in A (cm ² /sec)	$\frac{D \text{ in H}_2}{D \text{ in A}}$
Carbon	14.8	30.6	11.0	2.8
Triatomic carbon	44.4	19.7	5.4	3.6
Tantalum (50)	(50)	16.7	4.2	4.0
Tantalum (100)	(100)	14.4	3.2	4.5

probably volatilized from the surface of the solid or liquid. Assuming that the diffusion coefficient for monatomic carbon applies, the use of argon would give a diffusion coefficient of 0.36 of that in hydrogen, and presumably the volatilization would also be about one-third as much. Also, carbon has a significantly higher diffusion coefficient than tantalum and would have a higher volatilization even if the decomposition pressures were equal. Fonda¹⁹ obtained a rate of volatilization of tungsten in nitrogen of about 1.5 times that in argon, while the ratio of the diffusion coefficients is about 1.15. Argon and hydrogen would be expected to have a considerably greater difference in vaporization rates, since hydrogen would give a diffusion coefficient of about 3 to 4 times that in argon.

If we use hydrogen as the inert gas, atomic hydrogen would amount to 0.17 of the gas at 3000°K, and it has diffusion coefficients approximately double those for molecular hydrogen. At 4000°K, atomic hydrogen is 0.77 of the hydrogen, and the use of hydrogen might give greater losses relative to the use of argon than is indicated by the diffusion coefficients in Table II.

c. Effect of Inert Gas Pressure

The effect of pressure of the inert gas on vaporization has also been studied by Fonda²⁰ and the vaporization decreased directly with the pressure for pressures greater than 0.15 atmospheres. The rate

of evaporation of a tungsten filament of 0.01 cm diameter at 2870°K was 230×10^{-9} g/cm² sec in vacuum and was 3.9×10^{-9} for 1 atmosphere of 86 percent argon-14 percent nitrogen--a reduction by a factor of 0.017. A 0.2-cm tungsten filament is estimated to have an evaporation rate at 1 atmosphere of 0.0022 of the rate in a vacuum. These values are in reasonable agreement with the value 0.010 to 0.001 found by Nadler (Fig. 5).

3. Application to Melt Growth Conditions

So far, the vaporization of tantalum carbide has been discussed in terms of the effect of temperature in vacuum, the vapor pressure of tantalum and carbon in a sample, the effect of sample diameter, choice of inert gas, and pressure of inert gas. However, most of the data apply below 3000°K, and an estimate is still needed of the change in composition of the sample from the volatilization at the melting point. It seems best to use an arbitrary factor to relate vapor pressure to vaporization rate, even though this may be an order of magnitude in error. Based on Fig. 5, the vaporization rate in helium is a factor of 100 to 1000 less than that in vacuum, or about a factor of 10 to 200 less than the numerical value of the vapor pressure in atmospheres. The data by Fonda showed the calculated vaporization rate of a tungsten 0.2-cm-diameter filament to be a factor of about 1000 less than the numerical value of the vapor pressure in atmospheres. For the rough calculation of change in composition, we shall assume that the vaporization rate in g/cm² sec is 0.01 of the numerical value of the vapor pressure in atmospheres. From Fig. 4, the estimated vapor pressure of carbon over liquid tantalum carbide is about 0.04 atmosphere at 46 atomic percent carbon and 0.08 atmosphere at 50 atomic percent carbon. This gives a carbon vaporization rate of 0.002 moles/cm²/min over liquid tantalum carbide at 46 atomic percent carbon and 0.004 moles/cm²/min at 50 atomic percent carbon. These rates of loss of carbon might well be an order of magnitude too high owing to the assumptions that were made. In addition, changes of the inert gas compositions may alter these rates by another order of magnitude.

The addition of acetylene may reduce the volatilization of carbon markedly. A mixture of 10 percent acetylene and 90 percent argon would produce an equilibrium pressure of carbon of about 0.022 atmosphere. The vapor pressure of carbon over tantalum carbide containing 46 atomic percent carbon at 4000°C is 0.04 atmosphere. A sample with about 43 atomic percent carbon is estimated to be in equilibrium with 10 percent acetylene. Use of a mixture of acetylene, hydrogen, and argon might decrease the possible deposition of carbon from the acetylene.

The results of these calculations indicate that the growth of single phase carbide crystals from the melt is quite feasible. The numbers obtained are very approximate but are certainly close enough to desired equilibrium values to force the issue to be resolved experimentally. It appears that one may not only be able to maintain the carbide within the single phase homogeneity range, but that it may be possible to maintain specific compositions within this range by proper control of the gaseous environment and the composition of feed powders.

4. Vaporization of Hafnium Carbide

The vaporization of hafnium carbide shows distinct differences from that of tantalum carbide. Figure 6 gives the vapor pressure and vaporization rate data by Coffman²² along with the calculated data by Kaufman.¹⁴ The experimental data by Coffman show that hafnium is the predominant vapor over HfC, while carbon is lost from TaC.¹² Also, the vaporization rate in vacuum at 3000°K is about 2.4 times as great for HfC as for TaC. The effect of composition is shown in Fig. 7, which indicates that HfC with 49.8 atomic percent carbon at 3000°K would be stable during volatilization in vacuum. In the presence of an inert gas, the faster diffusion of carbon might result in a stable composition of 49.6 atomic percent carbon. Further, the vaporization rate would be a minimum at these stable compositions. At the melting point, the relative vapor pressures of carbon and hafnium would differ from those for the solid at 3000°K, but the general trends that are found for the solid will also show up in the liquid.

The problem in melting hafnium carbide is more likely to be due to the greater volatilization rather than to changes in composition. If such proves to be true experimentally, the use of a very slow flow rate of argon should be advantageous.

D. Melt Growth

1. Arc Fusion

Based on the above considerations, a series of test runs were made to examine the stoichiometry shifts resulting from melting of HfC and TaC in various environments. For this work, the two-electrode a-c arc furnace described in the previous report was employed. Firth Sterling HfC powder was hot-pressed at 3500 psi and 2300°C, as recommended by Sanders and Grisaffe,²³ to form disks 1 inch in diameter and 0.1 inch thick with a density approximately 85 percent of theoretical. These were then cut to form rods 0.1 inch square and 1/2 to 1 inch in

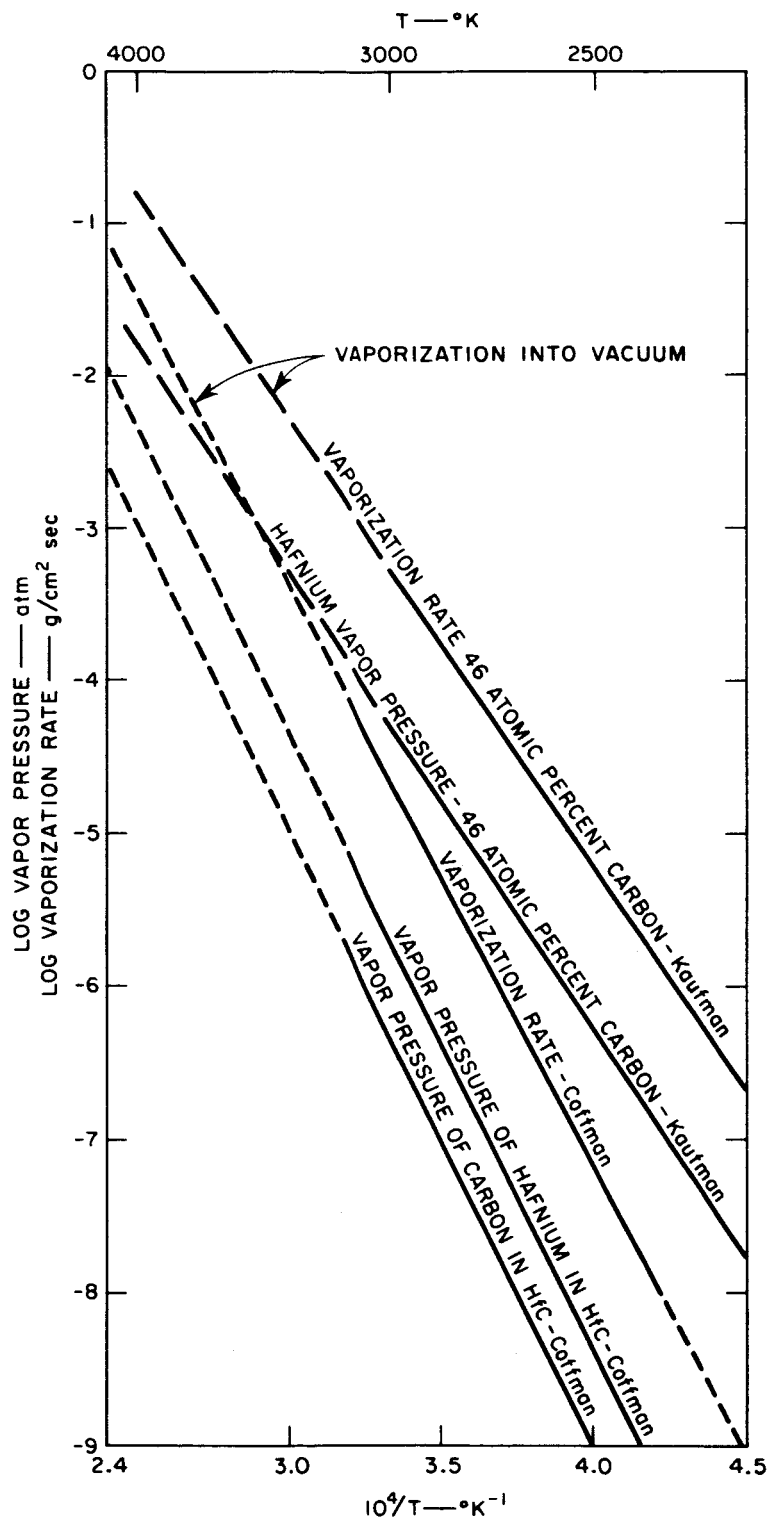


FIG. 6 VAPOR PRESSURE AND VAPORIZATION RATE FOR HAFNIUM CARBIDE

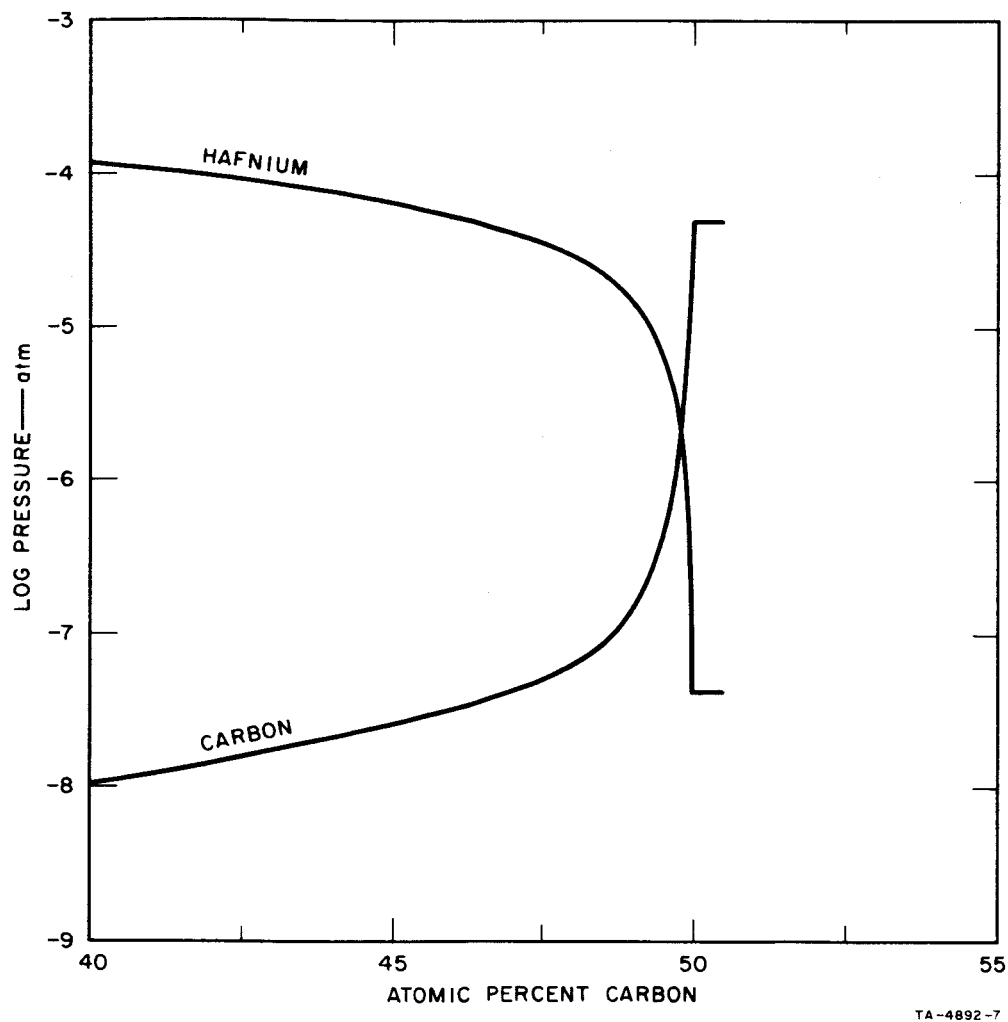


FIG. 7 CALCULATED VAPOR PRESSURES OF Hf AND C OVER HfC
AT 3000°K (Kaufman¹⁵)

length. Kennametal TaC was plasma-sprayed into copper molds to form rods 0.1 by 0.1 by 2 inches at approximately 75 percent of theoretical density.

These rods were then mounted on a graphite chuck, which was, in turn, mounted in the water-cooled seed rod holder in the arc furnace. After the desired atmosphere was admitted to the furnace, the arcs were formed, and the power level was increased until a large molten cap was formed at the top of the carbide rod. The melt was maintained for from 1 to 5 minutes. The sample was then quenched and cut along the center of the bead, perpendicular to the seed rod axis. The top portion (melt cap) was ground for X-ray evaluation, and the cut face of the lower portion was polished for metallographic study. The results of X-ray examination are shown in Table III, and polished sections are shown in Figs. 8 and 9.

Table III

LATTICE PARAMETERS OF ARC-MELTED CARBIDES

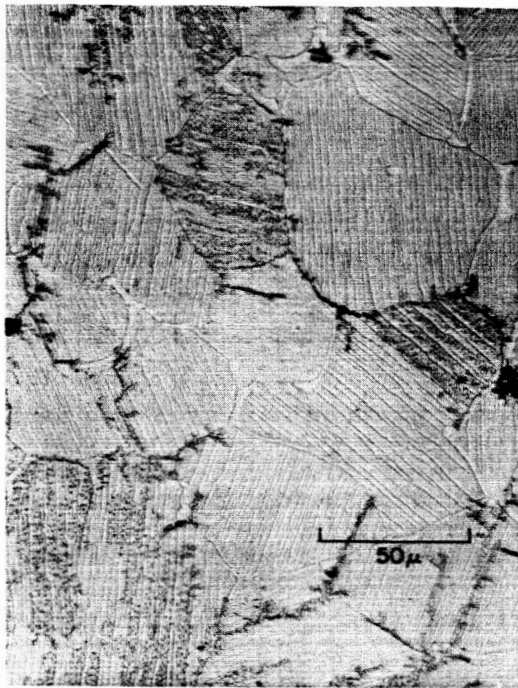
Specimen Number	Treatment	a_0 (Å)
TaC-P	Starting Powder	4.449 ± 0.001
TaC-PS	Plasma Sprayed	4.439 ± 0.002
TaC-1	Melted in Argon 1 min	indeterminate ^a
TaC-2	Melted in Argon 5 min	4.418 ± 0.002^b
TaC-3	Melted in Hydrogen	4.436 ± 0.002^c
TaC-1	Melted in 95 Argon, 5 Acetylene	4.414 ± 0.002^d
HfC-P	Starting Powder	4.631 ± 0.001
HfC-HP	Hot-Pressed	4.632 ± 0.001
HfC-1	Melted in Argon	4.618 ± 0.002
HfC-2	Melted in Hydrogen	4.642 ± 0.001
HfC-3	Melted in 70 Argon, 30 Hydrogen	4.633 ± 0.001
HfC-4	Melted in 95 Argon, 5 Acetylene	4.640 ± 0.001

^a More Ta₂C than TaC

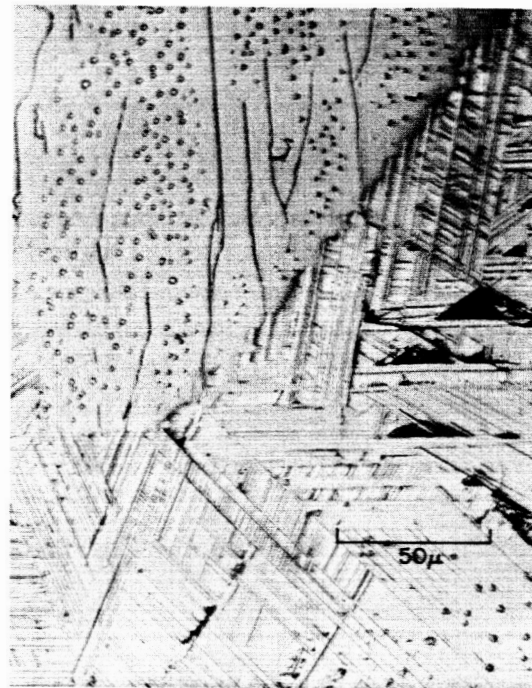
^b More TaC than Ta₂C

^c No Ta₂C detected (< 5%)

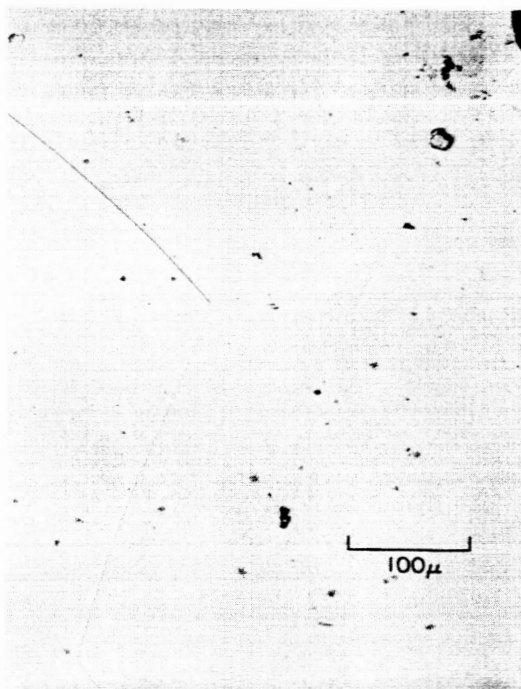
^d Very little Ta₂C



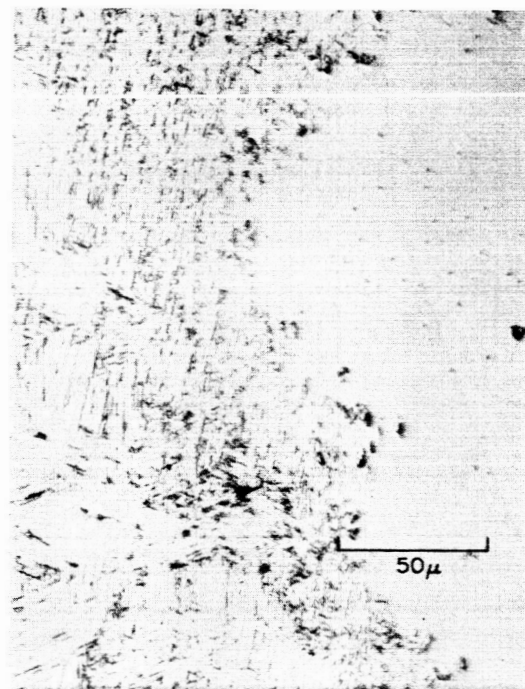
(a) TaC-1



(b) TaC-2



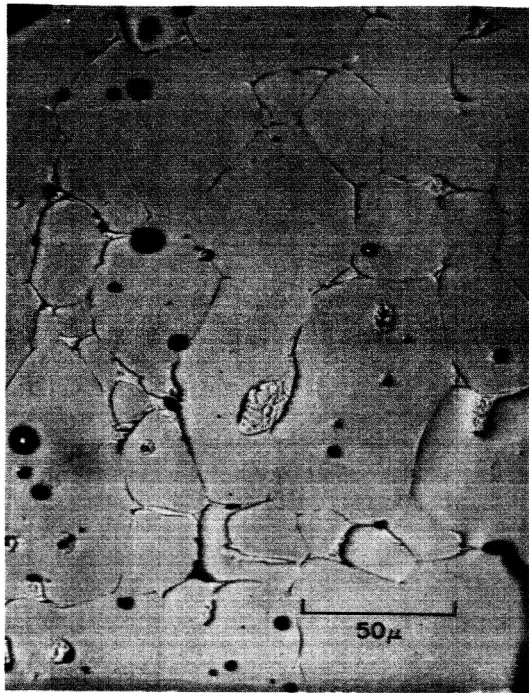
(c) TaC-3



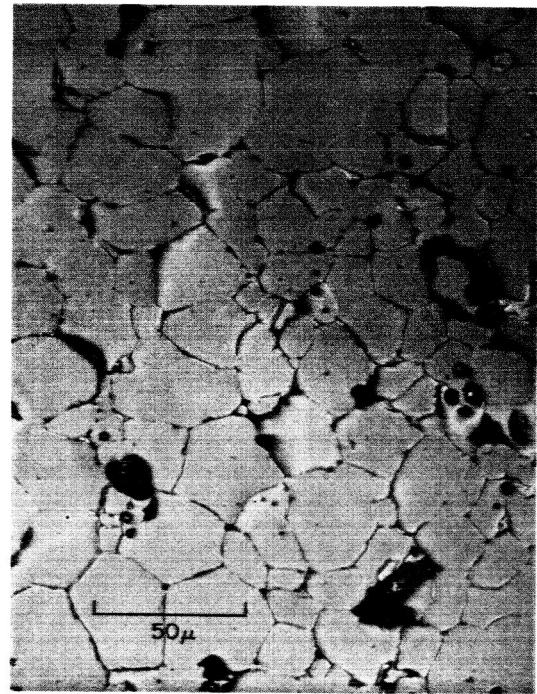
(d) TaC-4

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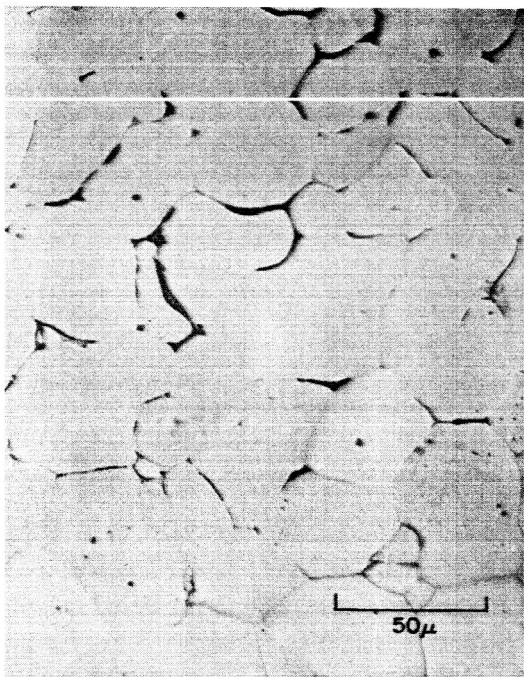
FIG. 8 STRUCTURE OF ARC-MELTED TANTALUM CARBIDE SPECIMENS



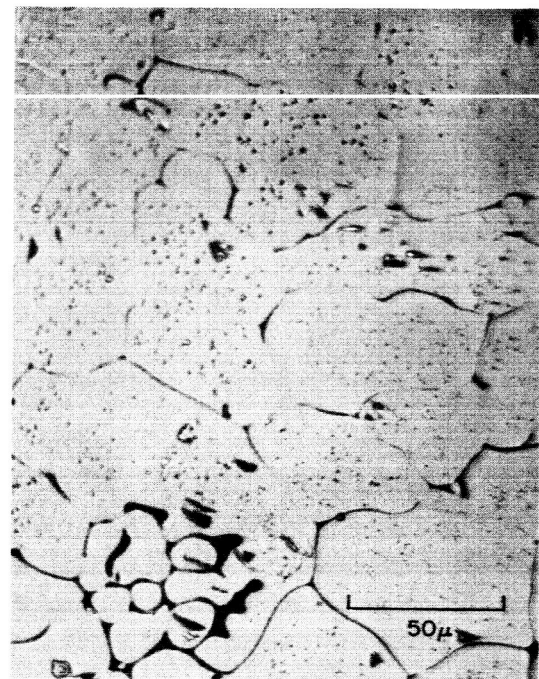
(a) HfC-1



(b) HfC-2



(c) HfC-3



(d) HfC-4

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FIG. 9 STRUCTURE OF ARC-MELTED HAFNIUM CARBIDE SPECIMENS

These results, although based on a very limited number of tests, are quite encouraging. If we compare the lattice constants obtained for tantalum carbide with Sara's values in Fig. 1, it appears that the starting material was slightly deficient in carbon (48.5 at. %). Additional carbon was lost during plasma spraying (< 47 at. %). Melting in argon shifted the composition to the two phase region, greatly lowering the TaC lattice parameter, and the small addition of acetylene did not reduce this effect significantly. However, the lattice constant remained unchanged during melting in hydrogen, as can be seen in Fig. 8c, a single phase recrystallized. This apparent contradiction to the results of thermodynamic considerations described in the preceding section, in which it was pointed out that the carbon loss should be greater in hydrogen than in argon, may arise from the heated carbon arc electrodes, which were close to the molten carbide. It remains to be seen how the stoichiometry can be shifted through the addition of acetylene to the hydrogen.

The starting hafnium carbide powder appears to have been somewhat low in carbon also, although the presence of boron may contribute to the low lattice parameter. Hot-pressing caused no shift in composition. Melting in argon again lowered the lattice parameter to a point found by Sara (Fig. 2) to correspond to the low-carbon side of the homogeneity field. This was the only HfC specimen found by optical examination to have a second phase. The dark boundaries in the other pictures in Fig. 9 are pull-outs and grain edges accentuated by etching. The addition of 30 percent hydrogen to the argon prevented any shift in the lattice parameter, and, when melting was performed either in pure hydrogen or in argon to which a small amount of acetylene was added, the lattice parameter increased to a value corresponding to nearly stoichiometric HfC.

2. Plasma Fusion

At the time the last report was prepared, it appeared that the problem of breaking the water-cooled plasma containment tubes had been solved. However, these continued to break during extended operation, so this design was not considered adequate for crystal growth. The connection of the plasma tube to the top of the annealing furnace was therefore changed to permit the use of quartz tubes for the inside wall. Since that time no tube failures have occurred. This change brought the metal top of the annealing furnace to within four inches of the r-f coil, and it was anticipated that some arcing or excessive heating might occur. However, no such difficulties have been encountered. It may be necessary to move these even closer in order to prevent excessive cooling of the crystal between the growth and annealing steps.

Initial melting experiments established that it is not possible to melt hafnium carbide in the argon plasma, operating with 10 kw in the load circuit. Work has now been initiated to attempt to improve heat transfer to the carbide by the addition of hydrogen to the plasma. Normally the presence of a diatomic gas plasma significantly improves heat transfer. (The success obtained in handling oxides results primarily from the use of oxygen-bearing plasmas.) If sufficient heat cannot be obtained by altering the plasma gas composition, it may be necessary to shift to a higher power generator.

E. Solution Growth

In attempting to develop solution growth techniques for preparation of carbide crystals, it is first necessary to find a suitable solvent liquid. This liquid must provide to a sufficient degree:

1. Solution of the crystal components
2. Variation of the solubilities of components with temperature
3. A continuous transfer of supersaturated solution to the growing crystal surface
4. No compound or solid solution formation with the crystal at growth temperatures
5. Ions or atoms that, if incorporated into the crystal, will not influence its useful properties
6. If possible, an ion in common with the solute, or, if not, one in which the ionic radii differ as much as possible from those of the solute
7. A low viscosity
8. A low vapor pressure, in order that desired compositions may be maintained
9. A lower melting point than that of the solute
10. Solubility in some medium which does not affect the synthesized crystal.

Based on these considerations, three molten metals were selected for initial evaluation as solvents--germanium, iron, and aluminum. Tantalum carbide has previously been reported to form in iron and aluminum melts.^{3, 24} All of these metals are known to form inter-metallic compounds with hafnium and tantalum, but very little information is available on the properties of these compounds. Aluminum and

iron also form carbides, but these can be dissolved relatively easily. Germanium has a very low carbon solubility and should act primarily as an inert solvent. Iron and aluminum, on the other hand, may act to raise the carbon solubility.

To examine the carbon solubilities in these alloys, the Czochralski crystal grower was set up with a blind-end quartz tube mounted on the seed rod. In operation, a melt having the desired solvent-hafnium ratio was prepared in a graphite crucible and allowed to equilibrate for one to two hours under a helium atmosphere. To take a sample, the pressure was lowered to about 5 mm Hg and the open end of the quartz tube was lowered into the melt. The pressure was then raised quickly to one atmosphere, forcing some of the melt into the tube, and the tube was raised into the upper furnace chamber to cool. The sample was removed through a small entry port and was replaced with a new sample tube. The furnace was then equilibrated at a new temperature and the process was repeated. Carbon and hafnium analyses on the samples were performed by a commercial laboratory.*

Selection of quartz as the sample-tube material limits the sampling temperature to about 1650°C . Since most of the alloys are not completely melted much below 1350°C , this permits sampling over only a 300°C interval. For this reason, data presently being obtained can be used to compare different solvents, but the analysis precision is such that little can be said about solubility variations with temperature. This range could be extended by using graphite tubes, but carbon solubility data at the low levels encountered would then be suspect without a careful calibration study.

The initial set of analytical data obtained is shown in Table IV. The carbon concentration of the pure germanium melt was below detection limits, agreeing with published values of Scace and Slack.²⁵ With the addition of 10 atomic percent hafnium, the carbon concentration obviously increased, falling in the range of 100 ppm. From the free energy of formation of hafnium carbide, one can calculate the equilibrium carbon concentration under these conditions to be about 75 ppm. Separation studies, however, eliminated germanium from further consideration as a solvent. It was found that any acid capable of dissolving germanium attacked hafnium carbide even more rapidly. Therefore, no crystals could be isolated.

*

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Table IV

CARBON SOLUBILITY IN POTENTIAL SOLVENT SYSTEMS

Sample No.	Starting Alloy Composition (atomic percent)	Sampling Temperature (°C)	Carbon (ppm)	Hafnium (atomic percent)
Ge 1	100 Ge	1355	< 10 [*]	---
Ge 2	100 Ge	1515	< 10	---
Ge 3	100 Ge	1650	11	---
GeHf 1	90 Ge-10 Hf	1345	29	14.3
GeHf 2	90 Ge-10 Hf	1500	280	
GeHf 3	90 Ge-10 Hf	1645	28	
AlHf 1	89 Al-11 Hf	1345	34	
AlHf 2	89 Al-11 Hf	1500	305	25.7
AlHf 3	89 Al-11 Hf	1645	236	
FeHf 1	90 Fe-10 Hf	1600	> 4%	

* < Less than minimum detectable quantity

The aluminum-hafnium alloy showed an even higher carbon solubility. Following the sampling run, the remaining melt was cooled slowly in a high temperature gradient. Excess aluminum was dissolved in HCl, leaving a large volume of thin crystalline platelets approximately 4 mm across. These were identified by X-ray diffraction and chemical analysis as HfAl_3 . They could be dissolved easily in a 50 percent HF solution, leaving a microcrystalline black powder. This material proved to be hafnium carbide with a lattice constant of $4.628 \pm 0.002 \text{ \AA}$, and a small amount of free hafnium.

If we tentatively accept Sara's values for lattice constant, shown in Fig. 1, this implies about 39 atomic percent carbon--not too far from the

phase boundary reported by Benesovsky and Rudy¹⁰ at 37 atomic percent carbon at 1550°C. Use of Benesovsky's values for lattice constant, however, would indicate a carbon concentration of 48 atomic percent.

In the iron run, a greatly increased carbon concentration was obtained, as anticipated. Unfortunately, dissolution of the crucible apparently proceeded along a flaw in the crucible so that it failed, and the melt, as it drained, destroyed the heater, thus terminating this set of runs.

Additional solubility runs will be required, using aluminum and iron solvents containing smaller quantities of the refractory metal before actual crystal growth runs are initiated.

IV FUTURE WORK

Studies during the next period will be concentrated in the following specific areas.

1. Establishment of melting conditions for HfC and TaC in the r-f plasma
2. Continuation of stoichiometry studies in arc-melted carbides, utilizing high purity powders and varying the ambient conditions
3. Continuation of solubility studies for evaluation of potential solvents for low temperature crystal growth.

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